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Optimization the efficiency Photovoltaic Solar Cells using synthesized TiO_2 semiconductor nanomaterials and functionalized Carbon Nanotubes.

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Abstract

In this project there were prepared solar cells using substrates of ITO on glass. The cell assembly was performed using carbon-ITO as cathode and, fourth types of anodes: (1) ITO-TiO_2 commercial particles, (2) ITO-TiO_2 thin film, (3) ITO-TiO_2+SWCNT (functionalized single wall carbon nanotubes), (4) ITO- TiO_2+ MWCNT (functionalized multi wall carbon nanotube), as anode respectively. For these types of solar cells was used solution organic dye Congo Red with ethanol, iodine electrolyte solution, between the two electrodes producing a photovoltaic cell Grätzel.

Studies of X-Ray diffraction (XRD) in the synthesized nanoparticles of TiO_2 showed peaks corresponding to anatase structure, with particle size of 10 nm, and large surface area of 6 m^2 / g, too these showed higher stability potential that TiO_2 commercial particle.

Preliminary studies showed that dye sensitized solar cell containing TiO_2 nanoparticules and SWCNT showed the higher potential. Observed too that, the surface resistance is higher in the MWCNT then in the SWCNT.

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Keywords: *semicondutor,nanoparticles, TiO_2, carbon nanotube, solar cells.*

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Introduction

The study of nanomaterials is an option that is taken in this paper to increase efficiency, using the Grätzel photovoltaic cell as an alternative to the silicon ones. Those are made by electrodes optically transparent as ITO or SnO_2-F, titanium dioxide (TiO_2) with dye (congo red), graphite and an electrolyte [2][3][5]. The electrons in the valence band of the dye can be excited and injected to the conduction band of the TiO_2, leaving holes. Those holes left in the pigment will be quickly filled with ions of iodine (I^-), which will aggregate to be transformed to I_3^-. This process occurs in the nanoporous surface in femtoseconds and the reverse occurs in the positive part of the solar cell, as it is shown in the picture (Fig. 1) [5]. The electron in the TiO_2 conduction band will take a path reducing its energy level until reaches the ITO and then follow the circuit until get back in the cell in the positive side turning the I_3^- in I^-[8]. The carbon is used in the cathode as a catalyzed, it helps capture the electron by the I_3^-.[5]

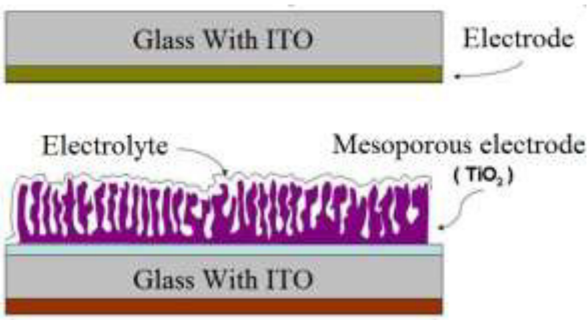


Fig. 1 Mouiting of cell Grätzel using TiO_2 nanoparticles, and functionalized single and multi wall NTC.

As mentioned before, the Dye-sensitized solar cell is a promising subject of studies, because of its low cost of production and considerable high efficiency[2]. However, it has not succeeded to be commercially competitive yet. To make these kind of solar cells competitive we have to increase their efficiency, usability and longevity. Usability and longevity can be obtained by a better form of maintaining the pigment without oxidize, also maintaining the electrolyte liquid.

Recombination of the ions of the electrolyte, injection and capture of electrons, conduction and photovoltaic effect are main studies to improve the efficiency of the dye-sensitized solar cells. The recombination as mentioned before is when the iodine accepts electrons, but it is not desirable to occur in the anode, because it uses an electron in the conduction band of the TiO_2 which have to reach the conductors [2-3][5-6]. Two approaches can be taken to inhibit recombination: (1) modify the surface of the titanium dioxide with certain materials, producing an energy gradient on the surface of the electrode to reduce recombination, and; (2) deposit oxide layer onto the TiO_2 surface to improve the performance.[2]

The main properties that make of the carbon nanotube (CNTs) a promising technology for many future applications are: extremely high strength, low mass density, linear elastic behavior, almost perfect geometrical structure, and nanometer scale structure [8]. They can be single-walled and multi-walled, which can diverge in some characteristics.

Experimental

In this project there were prepared solar cells using substrates of ITO on glass. The cell assembly were performed using carbon-ITO as cathode and, fourth types of anodes: (1) ITO-TiO_2

commercial particles, (2) ITO-TiO_2 thin film, (3) ITO-TiO_2+SWCNT (functionalized single wall carbon nanotubes), (4) ITO- TiO_2+ MWCNT (functionalized multi wall carbon nanotube), as anode respectively. For these types of solar cells was used solution organic dye Congo Red with ethanol, iodine electrolyte solution, between the two electrodes producing a photovoltaic cell Grätzel.

The deposition of carbon nanotube (CNT) on the substrate with ITO is accomplished using the technique provided by the collaborator Diniz et al [9], the electrophorese deposition (EPD). It was applied an electrical potential difference of 10V in a water dispersion of acid functionalized SWCNT and MWCNT, in pH 7. Before depositing the functionalized, that means to cut the extremity of the tubes by chemical breaking, as it is shown in the Fig.2 . The edges will be negative thanks to the carboxyl or sulfonated groups formed, making possible the deposition in the catode as shown in the Picture (Fig. 3).

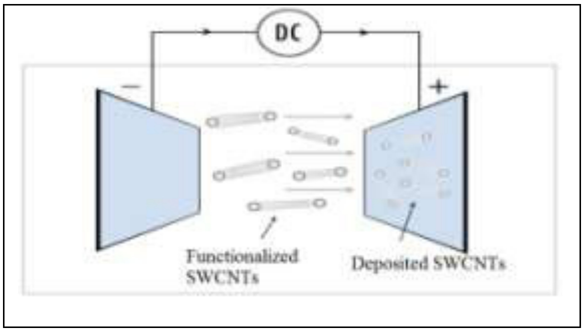


Fig. 2. System for Electrophorese deposition (EPD), development into Laboratory FGA-UnB.

The experimental procedure consists in add Carbon Nanotubes in nitric acid with concentration of 7M. 39mg SCNT (single-walled Carbon Nanotubes) with 36ml of HNO_3. The mixture have to pass in the process of reflux which is done by putting the mixture in the system of reflux. Carboxyl groups are created in the extremity of the Nanotubes by oxidation, the length is determined by the time of reflux.

The SCNT must be purified of the amorphous carbon. It was used a centrifuge with small tubes with the reflux prodct and spinned at 3000rpm for 15 minutes until the Nanotubes sediment. The superior liquid is drained then distilled water is added and the procedure is repeated. The procedure has to be repeated until the mixture have the pH value higher than 2. It is added KOH by dropping and measuring pH to reach the value 7. [12]

The deposition of the thin film of TiO_2 in the coated electrode was performed using TiO_2 resin synthesized by Pechini's method [10]. The technique was performed reacting citric acid with titanium isopropoxide and addition of ethylene glycol, the chelating agent, 40/60%, in mass, in relation to citric acid.

The first step is to prepare titanium dioxide citrate, which was obtained by the reacting citric acid with titanium isopropoxide for 24 hours at 80ºC, under constant agitation, until it turned to homogeneous system, this is the condensation reaction. Then, the ethylene glycol was added in small portions. The mixture was heated until it reaches 110 ºC, occurring the polyesterification forming an viscous polimeric resin, soluble in water. This resin is deposited in the electrodes with ITO (with or without SWCNTs and MWCNTs) with a paint-brush covering the entire surface, then was taken to the muffle furnace where was heated at 460 ºC. The result is a thin nanoporous electrode thin layer of ITO, TiO_2 and, if previously deposited, carbon nanotubes.

X-Ray diffraction (XRD) was used to analyze the structure and morphology of the TiO_2 particles used in the research.

The crystallite size (D_{RX}) was calculated through the Debye-Scherrer (Equation1) by measuring of the β enlargement in the half height of the peaks of diffraction of the anatase (TiO_2). The instrumental contribution to the enlargement (β') of X-rays diffraction was determined used as external standard hexaborato of lanthanum (θ= 15.2^o in the peak (110). [13]

$$D_{RX} = \frac{K\lambda}{(\beta^2 - \beta'^2)^{\frac{1}{2}} \cos\theta} \quad (1)$$

Equipment Thermo - Nicolet™ NXR FT-Raman Spectrometers was used in the Laboratory of Criminalist Institute, Federal Policy- DF-Brazil, with the supervision of Dr Márcio Talhavini.

The surface resistance of the anode, without TiO_2, was measured by four point resistivity technique Agilent B1500A Semiconductor Device Analyzer was used in the Solar Nanocells Laboratory of FGA-UnB. The technique consists in applying a gradually increasing current at four points, the square edges, of the surface. There were tested the samples with ITO, ITO+ SWCNT and ITO+MWCNT, both functionalized.

Results and discussion

According to the R-X difractograms, Fig.3, the nanoparticles of TiO_2 synthesized by Pechini´s method and calcinated at 700°C for 15 hours correspond to crystalline structures of anatase. Increasing the temperature to 800°C, the concentration of rutile is predominant and when it reaches 900°C the crystalline structure just corresponds to rutile. As observed that the mean crystallite size calculated using the *Scherrer* equation [1], shows a significative increase from 39 to 55 nm, when increasing the temperature from 700ºC to 900ºC. Also, it was verified that the superficial areas corresponding to this temperatures were 6m^2/g and 1m^2/g respectively.

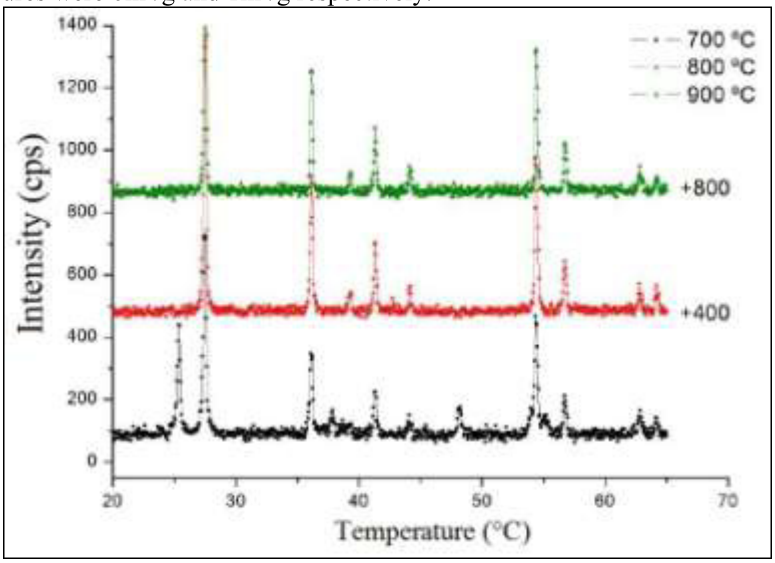
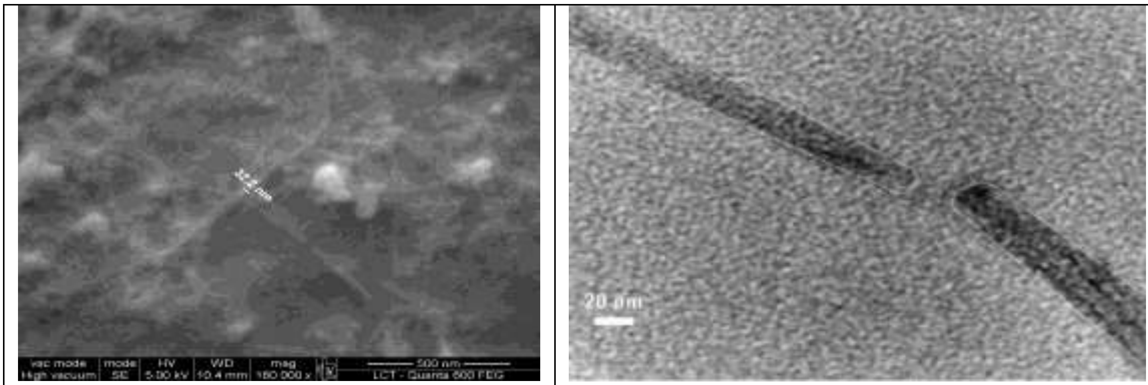


Fig. 3. R-X difratograms of TiO_2 nanoparticles, calcinated at: (a) 700 °C , (b) 800°C and (c) 900°C.

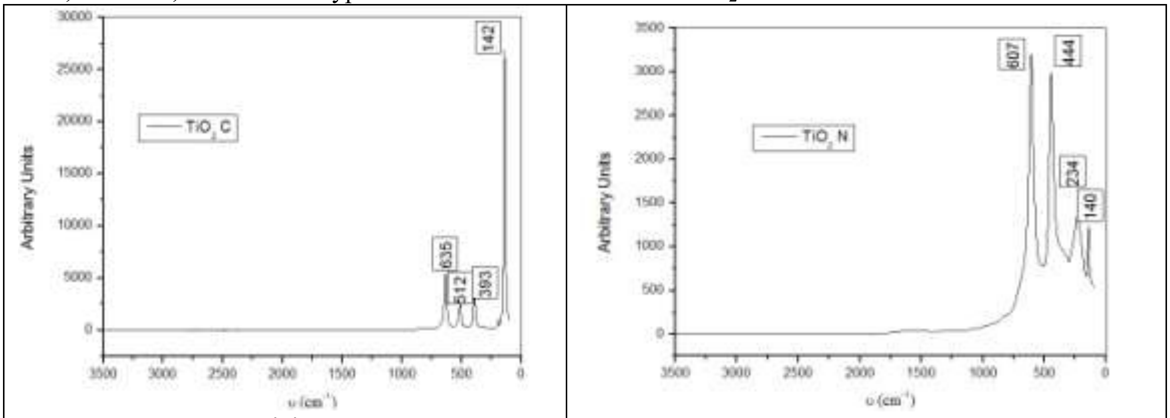
Using Scanning Electron mMicroscopy (SEM) Figure 4 (a) was observed morphologic the film of SWCNT Functionalities deposited on ITO substrate, too was noticed that this film showed small diameter (32 nm). Using technical High Resolution Transmission Electron Microscopy (HRTEM) Figure 4 (b) was observed the broken ends of SWNTC, this material is shortened and the amount of carboxylic acid functionalities is increased. We confirm that the diameters of the NTC are small (20 nm).



(a) (b)

Fig. 4. (a) SEM image of SWCNT on ITO substrate, and (b) HRTEM image of SWNTC Functionalities.

Raman spectra Fig. 5 (a) correspondents' to commercial TiO_2 shows four characteristic bands at 635 cm $^{-1}$, 512 cm $^{-1}$, 393 cm $^{-1}$ and 142 cm $^{-1}$ typical of the rutila structure of TiO_2. Raman spectra Fig. 5 (b) of TiO_2 nanoparticles synthesized in the laboratory shows four bands characteristics to 607 cm^{-1}, 444 cm^{-1}, 234 cm^{-1}, and 140 cm^{-1}typical of the anatase structure of TiO_2.



(a) (b)

Fig. 5- FT-Raman Spectra's: (a) Commercial particles of TiO_2 and (b) nanoparticles de TiO_2 obtained by Pechini´s Method.

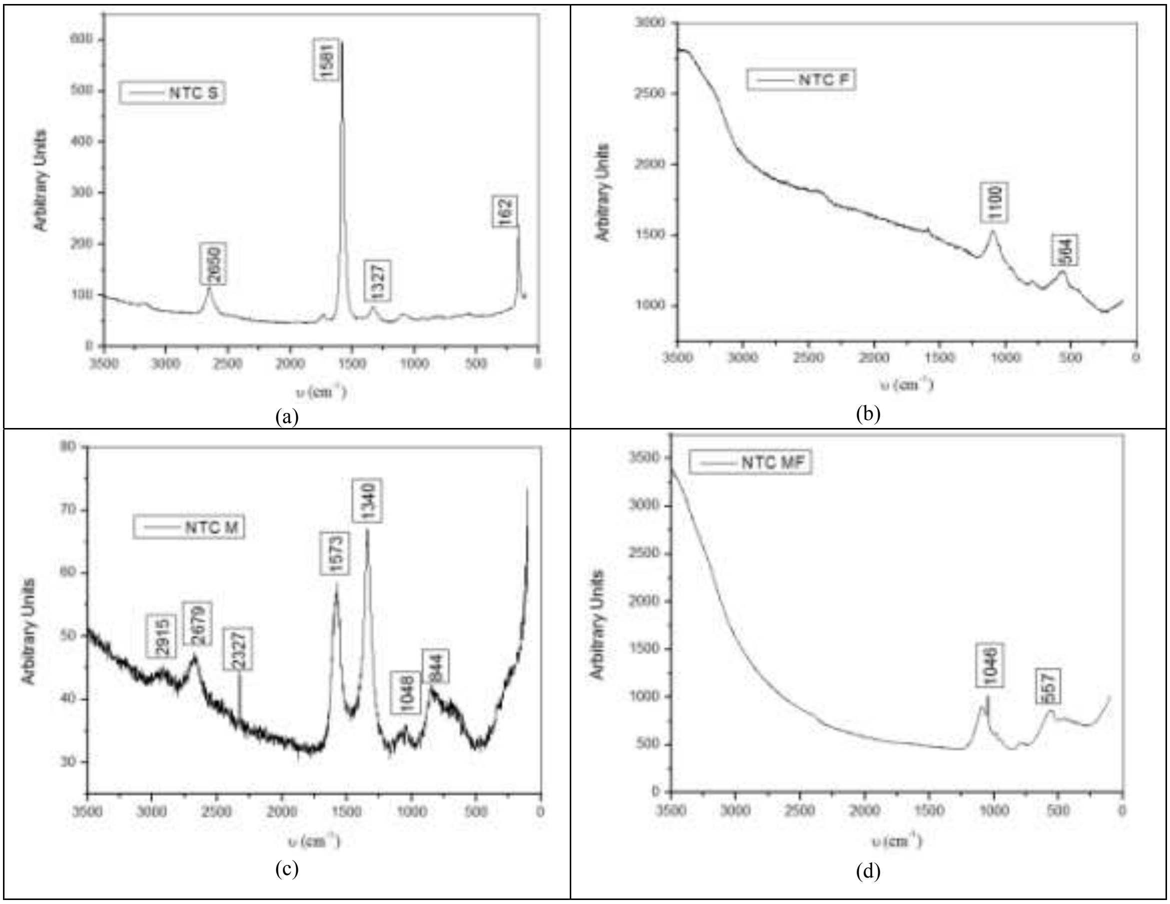


Fig.6. FT-Raman Spectra's of: (a) Single wall carbon nanotube-SWCNT, (b) SWCNT Functionalities, (c) Multi wall carbon nanotube-MWCNT, (d) MWCNT Functionalities.

In the figure 6 (a), the Raman spectra of the SWCNT (NTCS) showed fourth typical bands at 2650 cm^{-1} (G' band), 1581 cm^{-1} (G band), 1327 cm^{-1} (D band) and 162 cm^{-1} (RBM's band). The Raman spectra of the figure 6 (c) corresponding to MWCNT (NTC M) showed three typical bands at 2900-2670 cm^{-1} (G' band), 1600-1500 cm^{-1} (G band) and 1340 cm-1 (D band) [14] . It was observed that the spectra corresponding to MWNTC showed rather noise, and also presents two additional bands at 1048 cm^{-1} and 844 cm^{-1} due to impurities such as amorphous carbon, fullerenes, and metal catalyst particles in this material [12] , since the Raman spectrum of SWCNT is thoroughly cleaned with characteristic peaks quite symmetrical.[15]

Raman spectra's the figures 6 (b) and 6 (d) correspondent's to SWCNT and MWCNT, both functionalities, showed characteristic bands at 1100-1046 cm $^{-1}$ and 564-557 cm $^{-1}$ typical of the functional groups C = O and COOH respectively, thus verified that the CNT material is shortened and the amount of carboxylic acid functionalities is increased, moreover was observed that these spectra's do not show notable differences.

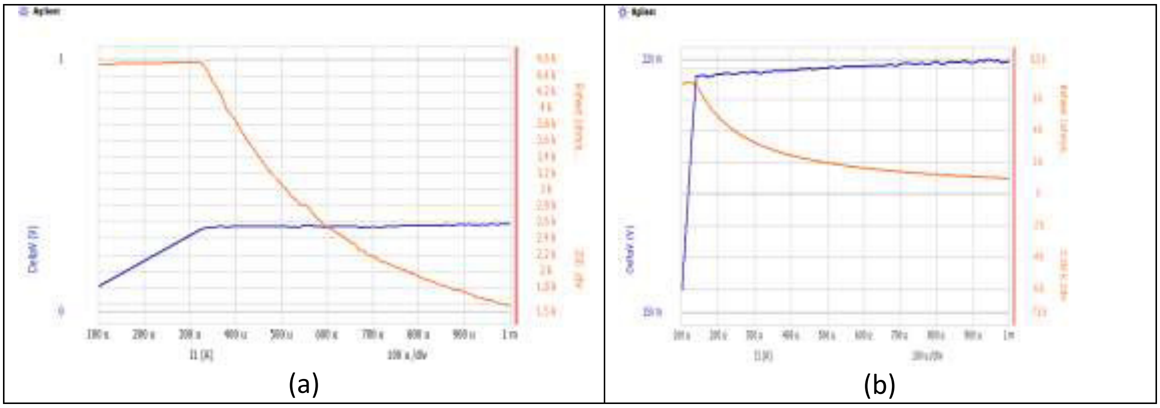


Fig. 7. Illustration and performance of ITO+SWCNT (a), and ITO+ MWCNT (b), both functionalized.

The graphic of the Fig.7 allows us to identify how the surface resistance and voltage changes as the current applied changes, which is a way to identify the higher conductivity of the samples constructed. The surface with ITO has a constant resistance of $9\Omega/cm^2$, knowing that the surface measures $9cm^2$. Comparing the surface resistance of ITO+SWCNT with ITO+ MWCNT, it is clear that at the initial and final points, at 100uA and 1mA, the surface resistance is higher in the MWCNT then in the SWCNT.

Acknowledgments

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